

IONICS CONDUCTION VIA CORRELATED BARRIER HOPPING MECHANISM IN CMC-SA SOLID BIOPOLYMER ELECTROLYTES

¹Z. Ahmad and ²M.I.N. Isa

^{1,2}Advanced Material Research Group, Renewable Energy Research Interest Group,
Department of Physical Sciences, Faculty of Science and Technology,
Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia.
Email: ¹za_fc@yahoo.com, ²ikmar_isa@umt.edu.my
Tel.: +609-6683111; Fax: +609-6694660

Abstract- The relationship between electrical and ionic transport properties has been investigated in the carboxymethyl cellulose (CMC)-salicylic acid (SA) system in the SA content range of 0–7 wt%. Furthermore, the dielectric permittivity (ϵ^*) and the modulus (M^*) permittivity properties of the CMC-SA system, as measured with electrical impedance spectroscopy (EIS) at ambient and elevated temperature have been explored. The conductivity of the CMC-SA was found to increase relatively to the SA content and temperature. The highest ionic conductivity at room temperature (303K) is $4.02 \times 10^{-7} \text{ Scm}^{-1}$ for sample containing 5wt% of SA and increases to $4.67 \times 10^{-6} \text{ Scm}^{-1}$ at 363K. The relation between the conductivity and ionic transport was linear. The conductivity was found to be capsized with the activation energy. The Correlated Barrier Hopping (CBH) is the best possible mechanism to present the hopping method in the CMC-SA system studied.

Keywords - ionic transport, dielectric behaviour, CBH mechanism, ionic conductivity

I. INTRODUCTION

Solid polymer electrolytes (SPEs) have gained technological importance as electrolytes materials for the solid state electrochemical devices such as batteries, fuel cells, electro chromic windows and super capacitors. Recently, SPEs are found to be advantageous compared to the conventional solid electrolytes in view of the flexibility, ease of preparation into required geometries and better electrode contacts. [1] Although, it has been studied by many researches, further improvements are needed. [2,3] Generally, solid polymer electrolytes has advantages over liquid electrolytes such as lightweight, improve leakage problem, mechanically stable and flexible for packaging design. Additionally, the performance of solid electrolytes based devices demands on the understanding of the mechanism of ions transport in its system. [4]

Previous researchers [5-7, 9-11, 13-14] have used casting technique as the method to produce thin films. The polymers were doped with various ionic doping material i.e. glycolic acid, ammonium salts, etc., which provide the ions for conduction. [6] This present study focused on developing carboxymethyl cellulose (CMC) doped with Salicylic Acid (SA) solid biopolymer electrolytes (SbPEs). CMC was chosen as it has good film forming property, high mechanical strength and can form a transparent film. [7,9] The employment of electrical impedance spectroscopy (EIS) method at wide frequency scale is to understand the frequency dependence of conductivity in various materials. [8] The effect of temperature [6, 7, 10, 11] and ionic transport properties [7, 10] was also studied. Finally, the conduction mechanism of the CMC-SA system was successfully determined.

II. EXPERIMENTAL

1.0 g of CMC (Across Organic Co.) was dissolved in 100 ml of distilled water until complete dissolution. Then, different amount of SA (in wt%) between 0–7 wt% was added and the mixture was stirred until the solution became homogenous. The solutions was poured into glass petri dishes and left dry at room temperature. The water free thin films thus obtained were further dried in the desiccators to discard any trace of water. The ionic conductivity of the samples was determined via Electrical Impedance Spectroscopy (EIS) using HIOKI 3532-50 LCR Hi-Tester in frequency of 50Hz–1MHz. The sample was placed between two stainless steel disk electrodes sample holder. The conductivity was studied at room and elevated temperature of 303–373K. The data collected contain complex impedance, admittance, permittivity and electrical modulus where it can be used for further analysis.

III. RESULT AND DISCUSSION

A. Conductivity and ionic transport study.

The conductivity of the SPE was calculated using data obtained from EIS with t is the thickness of the sample; A is the area of electrode-electrolyte contact and R_b is the bulk resistance of the equation below:

$$\sigma = \frac{t}{R_b A} \quad (1)$$

The sample designation, t , A and R_b is tabulated in Table 1. The conductivity calculated is shown in Figure 1.

Publication History

Manuscript Received : 12 August 2012
Manuscript Accepted : 23 August 2012
Revision Received : 25 August 2012
Manuscript Published : 31 August 2012

Table 1: Sample designation, t , A and R_b of the CMC–SA system prepared in this work.

Sample	Thickness, t (cm)	Electrode-Electrolyte Area, A (Cm ²)	Bulk Resistance, R_b
CMC-SA 0	0.0036	3.142	1.30 x 10 ⁴
CMC-SA 1	0.0043	3.142	1.00 x 10 ⁴
CMC-SA 2	0.0070	3.142	1.02 x 10 ⁴
CMC-SA 3	0.0030	3.142	7.08 x 10 ³
CMC-SA 4	0.0070	3.142	9.38 x 10 ³
CMC-SA 5	0.0063	3.142	5.00 x 10 ³
CMC-SA 6	0.0063	3.142	1.46 x 10 ⁴
CMC-SA 7	0.0053	3.142	1.40 x 10 ⁴

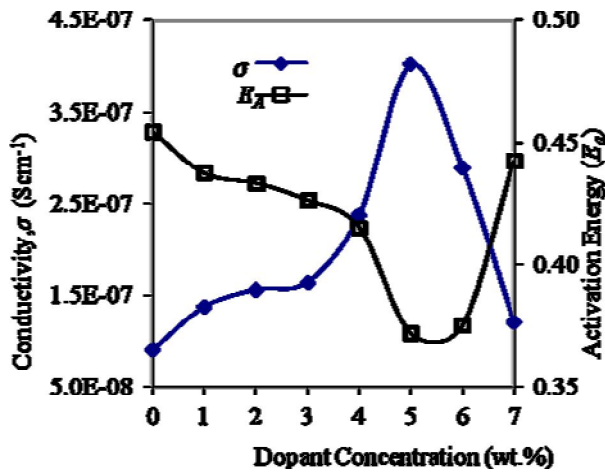


Fig. 1: Graph of conductivity and activation energy versus concentration of ionic dopant.

The conductivity depicted in Fig. 1 shows that by increasing the ionic dopant content will increase the conductivity from 0 wt% to 5 wt%. The highest conductivity obtained is $4.02 \times 10^{-7} \text{ S cm}^{-1}$ for sample containing 5 wt% of SA at room temperature. The increment of ionic conductivity was affected from the ionic mobility [2] via interaction between CMC and SA. The conductivity decreases above the addition of 5 wt% SA content and can be related to the re-association of the ions [5] which leads to the formation of ion cluster and thus decrease in the number of charge carrier and mobility due to the dipole interaction between the proton ions

in the medium increase attributable to higher ionic dopant concentration [6].

The study on mechanism of ionic conduction was examined via the conductivity-temperature dependent study. The Arrhenius plot [6] of $\log \sigma$ vs $1000/T$ was constructed for various composition of CMC–SA system in temperature ranges from 303–383K and depicted in Figure 2. The conductivity–temperature relationship of the SbPEs obeys Arrhenius behaviour where regression value is almost unity ($R^2 \sim 1$) and can be considered by the relation [8]:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \quad (2)$$

where σ_0 is the pre-exponential factor, E_a is the activation energy and k is the Boltzman constant. From this relationship, the value of E_a were calculated for all the prepared SPE by linear fit of the Arrhenius plot, where m is the slope of the Arrhenius plot. The calculated value of E_a is depicted in Fig. 1.

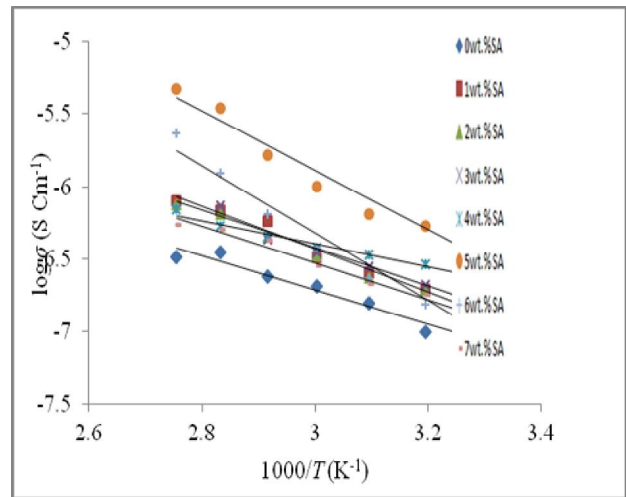


Fig. 2: Temperature dependence of ionic conductivity.

Principally, activation energy, E_a is the energy required for an ion to initiate movement. When the ion has acquired sufficient energy, it is able to break away from the donor site and move to another donor site. [5] It can be observed from Fig. 1, the values of activation energy were reflected to the conductivity. The differences of E_a can be related to the polymer segmental movement due to the ions transfer. The values of E_a for CMC–SA studied in this work are in range of 0.45 to 0.37 eV. The electrolytes with lower value of E_a implies that rapid ionic conduction occur in the CMC–SA system and hence elevates the conductivity. [10] The number density of mobile ion, n in this electrolyte has been calculated based on the Rice and Roth model: [6]

$$\sigma = \frac{2}{3} \left[\frac{(Ze)^2}{kTm} \right] n E_a T \exp\left[\frac{E_a}{kT}\right] \quad (3)$$

In equation 3, Z , E_a , and m is the valency, activation energy and mass of the conducting ion, respectively. T is absolute temperature, k is Boltzmann constant and e is electron charge, τ is the time for an ion to travel between sites. By knowing n and the conductivity, σ value, the mobility of the

ionic charge carrier, μ and diffusion coefficient, D can be calculated for every sample as follow [7]:

$$\mu = \frac{\sigma}{nq} \quad (4)$$

$$D = \frac{kT\sigma}{ne^2} \quad (5)$$

where, q is the number of electrons.

Fig. 3 show the normalised ionic transport properties which can be explained based on two (2) regions as follows:

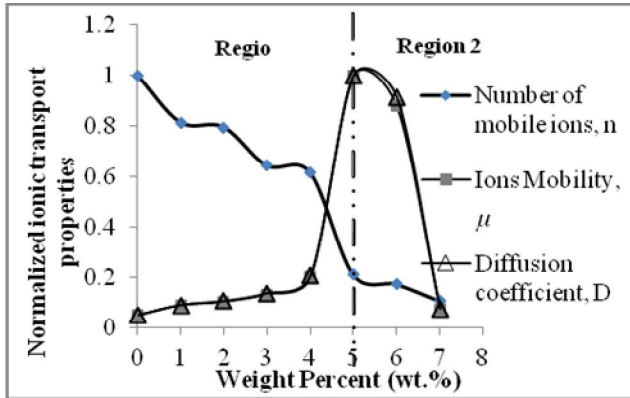


Fig. 3: Normalised ionic transport properties versus weight percent.

Region 1 (0–5wt% of SA): in this region, the conductivity increases with the addition of 1–5wt% of SA consequently increase the value of μ and D . The number density of mobile ion, n is mainly related to the change in free ion concentration [10]. The increasing conductivity is in contrast to the value of n , which means that the conductivity does not affected by the number of associate–disassociation of the ionic dopant in the polymer matrix. Contrary to n , the values of μ and D seem to tag on closely to the conductivity values. It can be inferred that the conductivity was mainly impinged on the ‘speed’ and ‘distribution’ of ions rather than the ‘amount’ of ions itself.

Region 2 (6–7wt% of SA): in this region, the value of n , μ and D decreases. The further decrease of n resulted in the decreased of total mobility therefore reduces the diffusion of ions thus, the space to ion ratio increases. As a result, the ion moves so rapidly and subsequently vibrate in its initial point thus reduces the conductivity even though the activation energy increased.

B. Dielectric Studies

The data collected via EIS contains complex impedance, admittance, permittivity and electrical modulus where it can be used for further calculation of the dielectric properties. The value can be derived as follow:

$$\epsilon = \epsilon_r + \epsilon_i \quad (4)$$

$$\epsilon_r = \frac{\epsilon_i}{\omega c_0 (\epsilon_r^2 + \epsilon_i^2)} \quad (5)$$

$$\epsilon_i = \frac{\epsilon_r}{\omega c_0 (\epsilon_r^2 + \epsilon_i^2)} \quad (6)$$

where $c_0 = (\epsilon_0 A) / t$, ϵ_0 is permittivity of free space. $\omega = 2\pi f$, f is frequency.

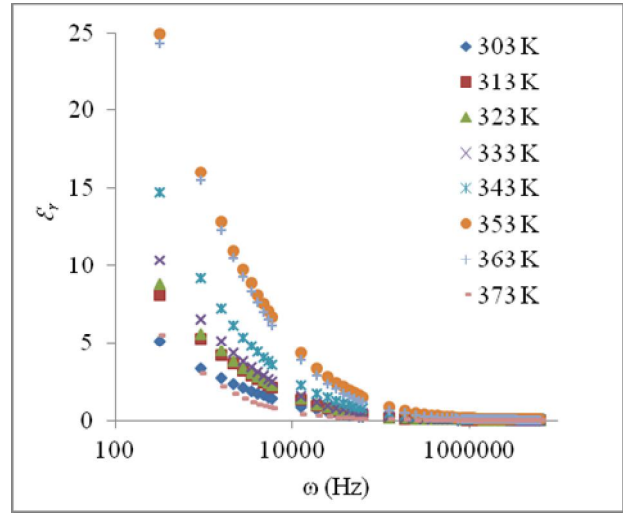


Fig. 4: ϵ_r versus ω (Hz) varied by temperature.

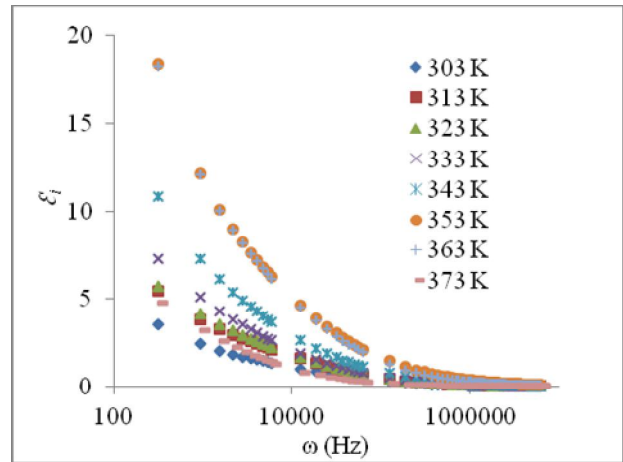


Fig. 5: ϵ_i versus ω (Hz) varied by temperature.

Referring to Fig. 4 and Fig. 5 of the dielectric constant (ϵ_r) and dielectric loss (ϵ_i) respectively, the trend is equally similar, where it rise sharply toward low frequency and decays at increasing frequency. It can be attributed to the electrode polarization effect which accumulation decrease relate with decreasing of both dielectric constant and dielectric loss. This is due to the periodic reversal of the

electric field occurs so fast at high frequencies because there was no excess ion diffusion in the direction of the field.^[2]

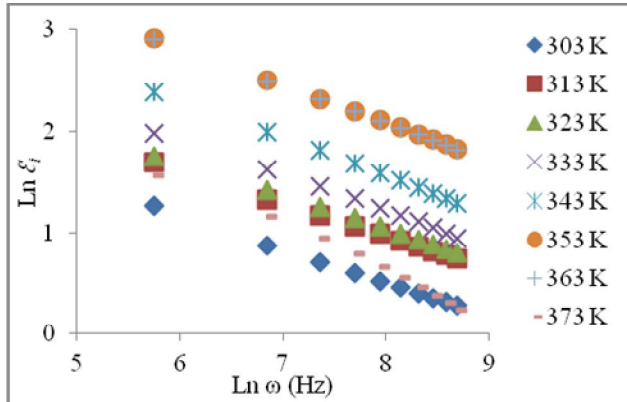


Fig. 6: Ln ϵ'' versus Ln ω (Hz) of varied temperature.

From the dielectric graph of Fig. 6, exponent s can be calculated from the slope at high frequency region.^[7] The acceptable range was at high frequency where there is no minimal space charge polarization. In this frequency, the electronic hops between pairs of sites can be explained when the relaxation process occur with local character.^[12] It was contributed by the superposition of the potential which yield a single ion potential that is actually felt by ion. The exponent s value was estimated using the relation $\sigma'(\omega) = A\omega^s$.

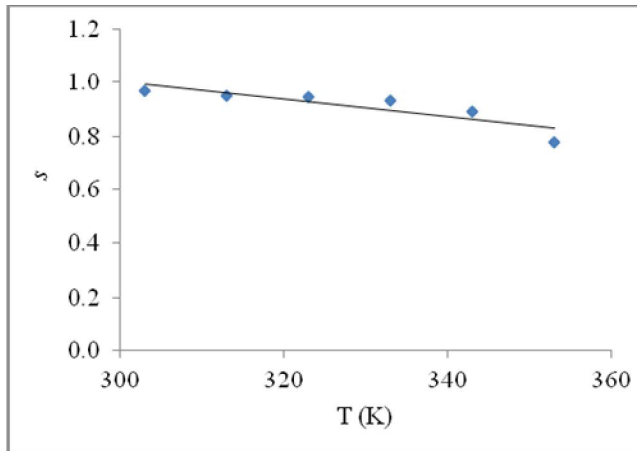


Fig. 7: Graph of exponent s versus temperature.

From Fig. 7, the value of s lies very close to unity (~ 1) and is independent of temperature.^[13] This behaviour/trend is best fitted to the Correlate Barrier Hopping (CBH) model, similar to that reported by Buraidah.^[5] For CBH model, it can be assumed that several potential as Coulombic repulsive potential were surrounded by the ions or charge carrier between many ions and a potential well in which the ions reside.^[5] In this model, two electrons are believed to simultaneous jump from one center to another center over the barrier separating the two sites, the barrier height, furthermore, being correlated with the interstice separation via the Coulombic interaction between centres.^[13]

C. Modulus Studies

The purpose of modulus (M) studies is to support the electrical conductivity data in previous section. The advantages of modulus studies were to recognize the conduction process and the effect on the frequency. The phenomena of modulus studies can be analyzed using equation below:

$$M_r = \frac{\epsilon_r}{(\epsilon_r^2 + \epsilon_i^2)} \quad (8)$$

$$M_i = \frac{\epsilon_i}{(\epsilon_r^2 + \epsilon_i^2)} \quad (9)$$

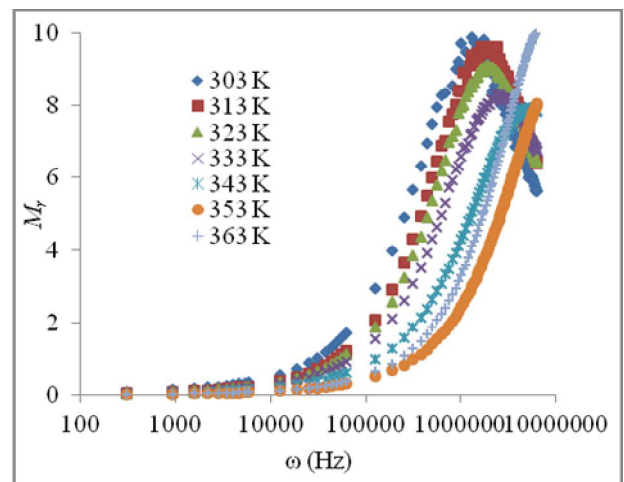


Fig. 8: Real part of dielectric modulus versus frequency varied by temperature.

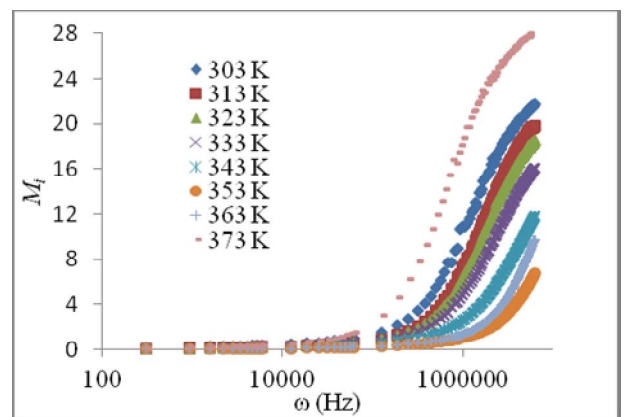


Fig. 9: Imaginary part of electrical modulus versus frequency varied by temperature.

Fig. 8 and Fig. 9 show the frequency dependence of the real part of dielectric modulus (M_r) and imaginary part of dielectric modulus (M_i) respectively. From the graph, M_r and M_i increase towards high frequency. The increasing electrical modulus can be related to the conductivity where at

the higher frequency shows that conductivity arises. Besides that, at higher frequency indicates the relaxation phase decrease with temperature and this may be due to the bulk effect.^[2, 14] With the increasing of temperature, the value of relaxation peaks shifted to higher frequency.^[2] The distribution of relaxation peaks is due to the distribution of relaxation time of the free charge.^[9] The existence of relaxation peak in real part modulus (M_r) formation of higher frequency indicating the polymer electrolytes films are ionic conductor.^[2] The relaxation peak do not exist in the M_i graph which is due to the residual water does not contribute toward conductivity enhancement.^[16]

The contribution of electrode polarization phenomena can be ignored at lower frequency of M_r and M_i . Furthermore, the tail was observed in lower part of frequency which indicates the samples are capacitive in nature for M_r and the distribution of relaxation time of the ionic conductor for M_i .^[14] The existence of the long tail can be considered as the result of the large capacitance associated with the electrode.^[15]

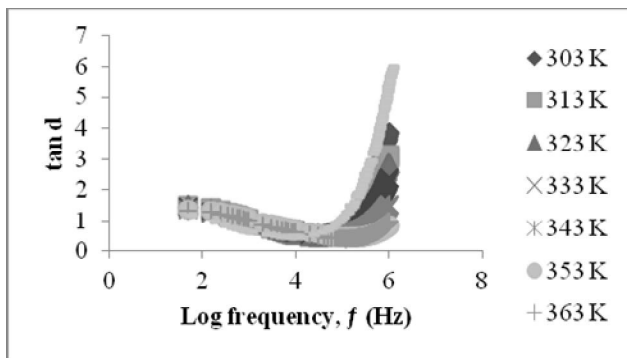


Fig. 10: tan d versus log frequency.

From Fig. 10, the peak of dielectric constant represents the relaxation time, τ . The graph of τ versus T was plotted and depicted in Fig. 11. The value of relaxation energy, E_r can be calculated from the slope of the graph. Contrary to E_A , E_r is the energy required for an ion to be in relaxes state. The values of E_r for CMC-SA studied in this work are in the range of 0.16 to 0.23 eV. In comparison to the E_A , the E_r is in the different range thus the ions hops at different energy potential which support the CBH model.

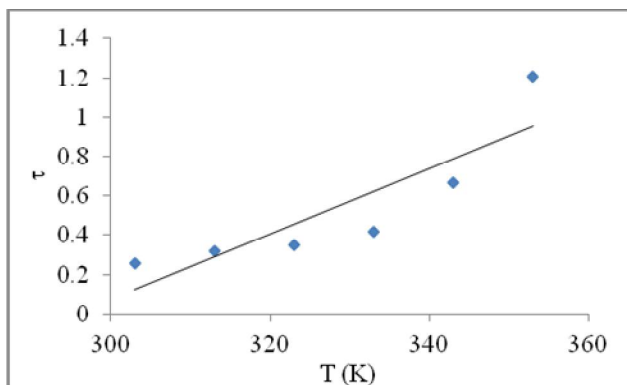


Fig. 11: Graph of τ versus temperature.

IV. CONCLUSION

The CMC-SA system studied in this work obtained the highest conductivity of $4.02 \times 10^{-7} \text{ Scm}^{-1}$ at room temperature. The conductivity increases with temperature following the Arrhenius behaviour. The activation energy for this system was capsized with conductivity value which is 0.345 eV obtained for the highest conductivity sample. The conductivity was found to be dependent on the ionic mobility and diffusion coefficient whilst the number of ions decreases with increasing temperature for all samples studied. The dielectric behaviour proved the CMC-SA system is an ionic conductor. The conduction mechanism was found to follow the CBH model as exponent s decrease with increasing temperature. The relaxation energy shows that it is in the dissimilar value range of the activation energy which supports the CBH model proposed for the CMC-SA system studied.

ACKNOWLEDGMENT

The authors would like to thank the MOHE for the Scholarship, the Department of Physical Sciences of the Faculty of Science and Technology, University Malaysia Terengganu, M.I.N. Isa, A.S. Samsudin, A.L.Azlan and M. N. Chai for all the helps, kind supports and courage given for this work to be successfully completed.

REFERENCES

- [1] Amrtha Bhide, Hariharan K, (2007), Ionic transport studies on $(\text{PEO})_6:\text{NaPO}_3$ polymer electrolyte plasticized with PEG_{400} , European Polymer Journal 43, pp. 4253-4270.
- [2] Ramesh S, Chai M.F. (2007), Conductivity, dielectric behaviour and FTIR studies of high molecular weight poly(vinylchloride)-lithium triflate polymer electrolytes, Material Science and Engineering B, vol. 139 pp.240-245.
- [3] Zhenglin Tang, Li Qi & Guitian Gao, (2008), Dynamic mechanical properties of gel polymer electrolytes containing ionic liquid, Solid State Ionics, Vol. 179, Issues 33-34, pp. 1880-1884.
- [4] Girish Kumar G, Sampath S, (2004), Spectroscopic characterization of a gel polymer electrolyte of zinc triflate and polyacrylonitrile, Polymer 45, p.p 2889-2895.
- [5] Buraidah M.H., Teo L.P., Majid S.R & Arof A.K, (2009), Ionic conductivity by correlated barrier hopping in NH_4I doped chitosan solid electrolytes, Physica B: Condensed matter, vol.404, Issues 8-11, pp. 1373-1379.
- [6] Nik Aziz N.A, Idris, N. K & Isa M.I.N (2010), Proton conducting polymer electrolytes of methyl cellulose doped ammonium fluoride: Conductivity and ionic transport studies, Int. J. of Physical Science Vol 5(6), pp. 748-753.
- [7] Nik Aziz N.A, Idris, N. K & Isa M.I.N (2009), Ionic conductivity studies of chitosan-based polymer electrolytes doped with adipic acid, Ionics, Vol 15, pp. 643-646
- [8] Samsudin A. S. & Isa M.I.N (2012), Structural and ionic transport study on CMC doped NH_4BR : A new type of Biopolymer Electrolytes, Journal of Applied Science 12 (2), pp 174-179.
- [9] Samsudin A.S & Isa M.I.N (2012), Structural and Electrical Properties of Carboxy Methylcellulose- Dedecyltrimethyl Ammonium Bromide-Based Biopolymer Electrolytes System, International Journal of Polymeric Material, pp 30-40.
- [10] Tan Winie, Ramesh S, Arof A.K, (2009), Studies on the structure and transport properties of hexanoyl chitosan-based polymer electrolytes, Physica B, pp 4308-4311.

- [11] Ramesh S, Arof A.K, (2001), Ionic conductivity studies of plasticized poly(vinyl chloride) polymer electrolytes, *Material science and Engineering B85*, pp. 11-15.
- [12] El Mkami H, Deroide B, Backov R, Zanchetta J.V, (2000) dc and ac Conductivity of $(V_2O_5)_x(B_2O_3)_{1-x}$ oxide glasses, *Journal of physical and chemistry of solids*, pp. 819-826.
- [13] S.R.Elliott, 1978, A.C. Conductivity Due To Intimate Pairs Of Charged Defect Centres, *State Communications*, Vol. 27, pp. 749-751.
- [14] Yahya M.Z.A, Arof A.K, (2003), Effect of oleic acid plasticiser on chitosan-litium acetate solid polymer electrolytes, *European Polymer Journal* 39, pp. 897-902.
- [15] Khair A.S.A, Puteh R, Arof A.K, (2006), Conductivity studies of a chitosan-based polymer electrolyte, *Physica B* 373, pp. 23-27.
- [16] Ramesh S, Tai Fung Yuen, Chia Jun Shen, (2008), Conductivity and FTIR studies on PEO-LiX [$x: CF_3SO_3^-, SO_4^{2-}$] polymer electrolytes, *Spectrochimica Acta Part A* 69, pp.670-675.
- [17] Osman Z, Ibrahim Z.A, Arof A.K, (2001), Conductivity enhancement due to ion dissociation in plasticised chitosan based polymer electrolytes, *Carbohydrate Polymer* 44, pp.167-173.
- [18] Uma T, Mahalingam T & Stimming U, (2009), Solid polymer electrolytes based on poly(vinylchloride)- lithium sulphate, *Material Chemistry and Physics* 90, pp. 239-244.
- [19] Shuhaimi N.E.A., Teo L.P, Majid S.R & Arof A.K, (2010) Transport studies of NH_4NO_3 doped methyl cellulose electrolyte, *Synthetic Metal* 160, pp. 1040-1044.
- [20] Woo H.J, Majid S.R, Arof A.K, (2011), Conduction and thermal properties of a proton conducting polymer electrolyte based on poly (ϵ -caprolactone), *Solid state ionic*, pp. 14-20.
- [21] Sankarappa T, Prashant Kumar M, Devidas G.B, Nagaraja N, Ramakrishnareddy R, (2008), AC conductivity and dielectric studies in V_2O_5 - TeO_2 and V_2O_5 - CoO - TeO_2 glasses, *Journal of Molecular structure* 889 pp. 308-315.
- [22] Qunyi Tong, Qian Xiao, Loong-Tak Lim, (2008), Preparation and properties of pullulan-alginate-carboxymethylcellulose blend film, *Food Research International* 41, pp1007-1014.
- [23] Chai M.I and Isa M.I.N, (2011), Carboxyl methylcellulose solid polymer electrolytes: ionic conductivity and dielectric study, *Journal of current Engineering Research*, Vol.1, issues 2, pp. 23-27.